

# DFT and TDDFT of mechanism in radical polymerization

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## ABSTRACT

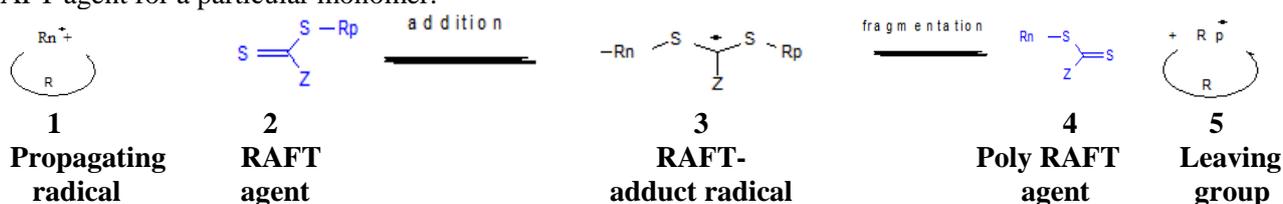
The reaction mechanisms; involved by thionocarbonates (O-(C=S)-O) and thionoesters (Z-(C=S)-O) compounds in reversible addition fragmentation chain transfer (RAFT) polymerization; were analyzed. Theoretical calculations were carried out by means of density functional theory (DFT), at B3LYP / 6-31G (d).

Two molecules of compounds detected intramolecular charge transfer (CT) band in absorption spectra which have been simulated using the Time dependent density functional theory (TDDFT). The lowest excitation energies ( $E_{\text{gap}}$ ) and the maximal absorption wavelength ( $\lambda_{\text{max}}$ ) of molecules are carried out at the optimized geometries of the ground states.

**KEY WORDS:** Radical polymerization, Density Functional Theory, Time-Dependant Density Functional Theory, Absorption Spectra.

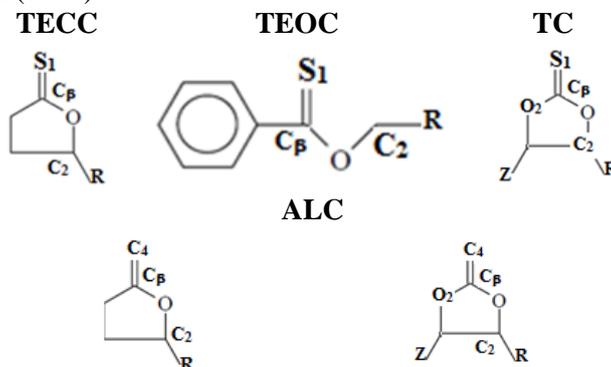
## 1. INTRODUCTION

The basic principle of the RAFT process is to protect the majority of the propagating species from bimolecular termination reactions through their reversible trapping into a dormant thiocarbonyl compound via the degenerative transfer reaction shown in Scheme-1. If R and Z are connected to form a ring structure, the result is a potential ring-opening monomer which provides general guidance on how to select the appropriate thiocarbonylthio RAFT agent for a particular monomer.



**Scheme.1. Reversible addition-fragmentation chain transfer (RAFT) polymerization**

Theoretical studies on the electronic structures of polymers have contributed a lot to rationalize the properties of known molecules and to predict those of yet unknown ones; helped us to provide an insight into structure-reactivity patterns in RAFT polymerization, and have led to the design of a new class of RAFT agent. Theoretical investigation on the band gaps of these compounds is very instrumental in guiding the experimental synthesis, which is the topic of the present work. The set of compounds chosen for this study are thionocarbonates (TC), thionoesters close cycle (TECC) and thionoesters open cycles (TEOC) with general structures (O-(C=S)-O) and (Z-(C=S)-O) respectively, and two alkenes (ALC) with structures (O-(C=C)-O) and (Z-(C=C)-O) (Figure.1). The aromatic ring introduces an extra basic site in the molecule. This well-known fact is at the very basis of the seminal studies on charge transfer by Benesi (1949); and Mulliken (1950).



**Figure.1. Schematic representation of monomers.**

**M1:** R = -CN, **M2:** R = -H, **M3:** R = -ph, **M4:** R=Z= -CN, **M5:** R = -CN, **M6:** R=Z= -CN, **M7:** R = -CN, **M8:** R = -CH<sub>3</sub>

Theoretical estimate of the interaction between methyl (R1), cyanomethyl (R2) and styryl (R3) radicals and a limited set of thiocarbonyl compounds, in order to better understand the reactivity in the addition – fragmentation reactions within the RAFT process. Of course molecular orbital calculations have been used to understand this

reactivity as well as the kinetics for these agents. Thermodynamic quantities at 298.15 K and the individual rate coefficients for addition and fragmentation reactions; between these different agents and methyl radical (R1); are compared at the same level of theory.

Finally, TD-DFT/B3LYP/6-31G (d) calculations of the lowest excitation energies and the maximal absorption wavelengths ( $\lambda_{\text{abs}}$ ) were then performed at the optimized geometries of the ground states and have been performed to examine the absorption spectra of molecules who present interesting thermodynamically results and the effect of several substituents on this, because the effects of substituents diminish rapidly with their distance from the reaction center.

## 2. METHODS

**Computational Details:** All calculations have been performed with the GAUSSIAN09 package of programs (Frisch, 2009) and all of our predictions of properties were calculated at the equilibrium geometry optimized at the DFT/B3LYP/6-31G\* level of theory (Becke, 1993; Hehre, 1986). The B3LYP method has been thoroughly tested by Riley (2007) and Tirado-Rives and Jorgensen (2008), on closed-shell organic molecules.

To understand the reactivity of these molecules, we examined the addition mechanism; of methyl radical; on a double bond C=S by calculating the global reactivity indices for each compound, such as the global electrophilicity index  $\omega$  given by Eq. (1) (Parr, 2004), which measures the stabilization in energy when the system acquires an additional electronic charge  $\Delta N_{\text{max}}$  from the environment, the electronic chemical potential ( $\mu$ ) in Eq. (2) and the chemical hardness ( $\eta$ ) in Eq. (3) of each system:

$$\omega = \mu^2/2\eta \quad (1)$$

$$\mu = -\frac{IP + EA}{2} \quad (2)$$

$$\eta = IP - EA \quad (3)$$

$\mu$  and  $\eta$  are derived from the ionization potentials and electron affinities given by:

$IP = E(N-1) - E(N)$  and  $EA = E(N) - E(N+1)$ ,  $N$  being the total number of electron of the native system, at its geometrical structure (Cimino, 2004). From the determined accurate geometries, frequencies and energies, gas-phase rate coefficients are obtained using the standard textbook formulae (Coote, 2004); Eq. (4)

$$k(T) = \kappa(T) \frac{k_B T}{h} (c^0)^{1-m} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (4)$$

Where  $k_B$  and  $h$  are Boltzmann's and Planck's constants respectively,  $R$  the ideal gas constant,  $m$  the molecularity of the reaction and  $\Delta G^\ddagger$  is the activation free energy of the considered reaction,  $c^0$  is the standard unit of concentration ( $\text{mol L}^{-1}$ ). The value of  $c^0$  were calculated for 1 mol of an ideal gas at 298.15 K and 1 atm, and hence,  $c^0 = 0.04087 \text{ mol.L}^{-1}$ .  $\kappa(T)$  is the tunneling coefficient which corrects for quantum effects in motion along the reaction path (Truhlar, 1996; Bell, 1980). It can be assumed to be negligible (i.e.  $\kappa(T) \approx 1$ ) for the addition of carbon-centered radicals to thiocarbonyl compounds (Latelli, 2014).

All vertical electronic transitions have been computed at the geometry of the singlet ground electronic state. Thus, the theoretical excitation energies correspond to vertical transitions which can be approximately identified as band maxima in experimental absorption spectra.

## 3. RESULTS AND DISCUSSION

**Descriptors and reactivity:** The ionization potential (IP), electron affinity (EA), electronic chemical potential ( $\mu$ ), chemical hardness ( $\eta$ ) are collected in Table I. First, qualitatively we can note that all computed chemical potentials of all compounds are higher than that of the cyanomethyl radical (R2) (-5.42eV) thereby indicating that, if any, a charge transfer will take place from nucleophile momomers compounds towards the cyanomethyl radical here acting as an electron acceptor. But the electronic chemical potential of methyl radical (R1) ( $\mu = -3.97\text{eV}$ ) is higher than that of M1, M4, M6-M8 ( $\mu$  between -3.99 and -4.69eV) and low than that of M5, M3, M2 ( $\mu$  between -3.74 and -2.98 eV). For the styryl radical (R3) there are also two face of charge transfer from monomers (M1- M3, M5, M6, M8) to styryl radical and from styryl radical (R3) to monomers (M4, M7). The results, as shown in Table 1, indicate that the two alkenes M5 and M6 are the hardest compounds, thus explaining their resistance to change their electronic distribution. Furthermore to thioesters results show that M2 is less susceptible to electronic change i.e. that has the highest hardness thereby showing that the presence of several benzyl groups greatly affects the stability of the agent by limiting its response. The effects of substituents on the RAFT agents are qualitatively different; agents are strongly stabilized by electron-donating Z substituents, and are strongly destabilized by electron-withdrawing groups (as CN) at the R position (Michelle, 2005). So, comparison  $\omega$  between M1, M2 and M3 shows that the monomer bearing the CN group, that delocalizes the unpaired electron, is more electron withdrawing.

According to the absolute scale of global electrophilicity power ( $\omega$ ) reported by Domingo (2002), the M4, M7 and M8 monomers can be classified as strong electrophiles whereas M1 and M3 displays a moderate electrophilicity power. Whereas R2 has a large electrophilicity power (1.56 eV) than R3 (1.03 eV).

Supplementary information (see Table 2) shows the electrophilicity difference ( $\Delta\omega$ ) and the fraction of transferred electron ( $\Delta N^o$ ) cited in Eq. (5) and Eq. (6) respectively:

$$\Delta\omega = \omega_{E^+} - \omega_{Nu} \quad (5)$$

$$\Delta N^o = \frac{(\mu_{Nu} - \mu E)}{(\eta_{Nu} + \eta E)} \quad (6)$$

**Table.1. Ionization potential (IP), electronic affinity (AE), electronic chemical potential ( $\mu$ ), chemical hardness ( $\eta$ ) and global electrophilicity ( $\omega$ ) (in eV)**

Monomers		IP	AE	$\mu$	$\eta$	$\omega$
TECC	M1	8.439	-0.368	-4.035	8.808	0.924
	M2	8.416	-1.005	-3.705	9.421	0.728
	M3	8.104	-0.622	-3.740	8.727	0.801
TEOC	M7	8.711	0.608	-4.660	8.103	1.340
	M8	8.200	0.110	-4.155	8.089	1.067
TC	M4	9.319	0.061	-4.690	9.257	1.188
ALC	M5	8.341	-2.387	-2.976	10.729	0.412
	M6	9.099	-1.117	-3.990	10.216	0.779
Radicals	R1	9.770	-1.803	-3.97	11.55	0.694
	R2	10.126	0.718	-5.422	9.408	1.562
	R3	8.823	-0.189	-4.316	9.013	1.033

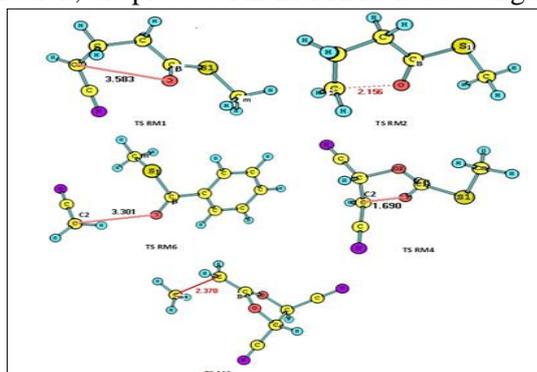
The interaction between R2 and monomers presents the highest value in the difference of electrophilicity ( $\Delta\omega$ ) as well as the fraction of transferred electron ( $\Delta N^o$ ) for all monomers only for monomer M5 which present the highest value of ( $\Delta\omega$ ) with R1(CH3). Those values ( $\Delta N^o$  and  $\Delta\omega$ ) indicate a larger polar character for the radical addition mechanism of R2/monomers than for the addition of R3/monomers and R1/monomers.

**Table.2. Fraction of transferred electron ( $\Delta N^o$ ) and electrophilicity difference ( $\Delta\omega$ )**

		M1	M2	M3	M4	M5	M6	M7	M8
R1	$\Delta\omega$	-0.230	-0.034	-0.107	-0.494	0.282	-0.085	-0.646	-0.373
	$\Delta N$	0.001	0.014	0.013	0.033	0.046	0.000	0.033	0.007
R2	$\Delta\omega$	0.638	0.834	0.761	0.374	1.150	0.783	0.222	0.495
	$\Delta N$	0.076	0.091	0.092	0.039	0.121	0.073	0.043	0.072
R3	$\Delta\omega$	0.109	0.305	0.232	-0.155	0.621	0.254	-0.307	-0.034
	$\Delta N$	0.015	0.033	0.032	0.020	0.067	0.017	0.020	-0.009

**Thermodynamics:** The calculation indicates that there is no transition state in the addition reactions for the agents (M1, M2, M4, M5, M7 and M8). Furthermore, the thermodynamics data of these reactions are found to be exothermic ( $\Delta E < 0$ ). The addition of R1 to the eight compounds is (thermodynamically) spontaneous ( $\Delta G < 0$ ). The unique transition state has been located for the alkene M6 agent that the activation energies show a small value ( $\sim 3$ ). (Table 3). The fragmentation is then the important step of the polymerization reaction mechanism. Table 3 shows the thermodynamics parameters for fragmentation reactions. We can see that the fragmentation reaction is exothermic ( $\Delta E < 0$ ) and that the mechanism involves a transition state only in M2, M3, M4 and M6 which are displayed in Figure-2. When comparing the activation energies computed for RCAF1 (Latelli, 2014) and RM4, the fragmentation is thus easier for RM4. Then, considering the complete polymerization process, (addition and fragmentation), the whole polymerization reaction appears to be easier for the M4 monomer.

The representation of the spin density, condensed to atoms, is used to locate the atom(s) carrying the radical character. Then, following the addition, the radical is localized primarily on the  $\beta$  carbon (0.62- 0.87). In the transition state structures (TSRMx) the spin density is mainly distributed between the  $\beta$  carbon and C<sub>2</sub> in RIM3, RIM4 and RIM6 (see Table 4). After fragmentation, the product RIMx-FRAG holds a highly localized radical in C2 carbon.



**Figure.2. Optimized geometries ( $A^\circ$ ) of the transition structures for addition and fragmentation reactions**

**Table.3.** Thermodynamics parameters (barriers ( $\Delta E^\ddagger$ , kJ mol<sup>-1</sup>), activation enthalpies ( $\Delta H^\ddagger$ , kJ mol<sup>-1</sup>) and Gibb's activation free energies ( $\Delta G^\ddagger$ , kJ mol<sup>-1</sup>) at 298.15 K of the addition-fragmentation reactions, all calculations performed with 6-31G (d) basis set. († not converged)

	addition			
	$\Delta E$	$\Delta E^\ddagger$	$\Delta H^\ddagger$	$\Delta G^\ddagger$
<b>M1</b>	-73.29	-8.98	-10.56	24.88
<b>M2</b>	-61.67	-50.34	-56.12	-7.00
<b>M3</b>	-61.59	-4.20	-6.10	31.30
<b>M4</b>	-61.49	-58.39	-64.25	-13.76
<b>M5</b>	-122.38	-119.30	-125.35	-77.01
<b>M6</b>	-134.14	3.68	0.76	42.60
<b>M7</b>	-86.95	-83.33	-88.39	-40.42
<b>M8</b>	-78.09	-64.41	-69.84	-20.34
	Fragmentation			
	$\Delta E$	$\Delta E^\ddagger$	$\Delta H^\ddagger$	$\Delta G^\ddagger$
<b>R1M1</b>	-85.29	-84.31	-83.80	-86.30
<b>R1M2</b>	-29.88	137.07	139.34	134.25
<b>R1M3</b>	-81.23	†	9.9 <sup>a</sup>	13.2 <sup>a</sup>
<b>R1M4</b>	-121.27	22.88	22.74	23.69
<b>R1M5</b>	-64.03	-20.28	-18.16	-25.67
<b>R1M6</b>	-108.25	27.87	27.70	28.43
<b>R1M7</b>	-60.67	-19.53	-17.16	-26.58
<b>R1M8</b>	7.16	†	†	†

**Table.4.** Spin densities and bond lengths during the fragmentation of R1Mx

		R1M1	R1M2	R1M3	R1M4	R1M5	R1M6	R1M7	R1M8
<b>R1Mx</b>	<b>C<sub>β</sub>-O</b>	1.391	1.380	1.386	1.394	1.396	1.397	1.379	1.366
	<b>C<sub>β</sub>-O2</b>				1.383		1.391		
	<b>C<sub>2</sub>-O</b>	1.436	1.441	1.444	1.429	1.427	1.422	1.433	1.443
	<b>C<sub>β</sub>-S<sub>1</sub></b>	1.730	1.732	1.755	1.775			1.764	1.770
	<b>C<sub>β</sub>-C<sub>4</sub></b>					1.491	1.495		
	<b>S<sub>1</sub>-C<sub>m</sub></b>	1.854	1.856	1.835	1.833			1.842	1.841
	<b>C<sub>4</sub>-C<sub>m</sub></b>					1.546	1.542		
	<b>d<sub>spin</sub>C<sub>β</sub></b>	0.79	0.77	0.76	0.70	0.87	0.80	0.63	0.62
	<b>d<sub>spin</sub>C<sub>2</sub></b>	-0.00	-0.00	0.00	0.00	-0.00	0.00	0.02	0.02
<b>TS-frag R1Mx</b>	<b>C<sub>β</sub>-O</b>	1.211	1.211	1.307 <sup>a</sup>	1.293	1.218	1.302	1.213	
	<b>C<sub>β</sub>-O2</b>				1.355		1.368		
	<b>C<sub>2...O</sub></b>	3.582	2.155	1.765 <sup>a</sup>	1.690	3.065	1.675	3.301	
	<b>C<sub>β</sub>-S<sub>1</sub></b>	1.798	1.812	1.783 <sup>a</sup>	1.788			1.862	
	<b>C<sub>β</sub>-C<sub>4</sub></b>					1.523	1.499		
	<b>S<sub>1</sub>-C<sub>m</sub></b>	1.826	1.826	1.821 <sup>a</sup>	1.830			1.841	
	<b>C<sub>4</sub>-C<sub>m</sub></b>					1.527	1.544		
	<b>d<sub>spin</sub>C<sub>β</sub></b>	0.00	-0.00	0.46 <sup>a</sup>	0.43	-0.00	0.53	0.00	
	<b>d<sub>spin</sub>C<sub>2</sub></b>	0.85	0.99	0.22 <sup>a</sup>	0.28	0.84	0.29	0.88	
<b>R1Mx-frag</b>	<b>C<sub>β</sub>-O</b>	1.210	1.210	1.211	1.209	1.217	1.208	1.220	1.217
	<b>C<sub>β</sub>-O2</b>				1.361		1.370		
	<b>C<sub>2</sub>-O</b>	4.293	4.325	3.245	3.146	4.270	2.847	3.213	4.275
	<b>C<sub>β</sub>-S<sub>1</sub></b>	1.803	1.812	1.805	1.775			1.799	1.807
	<b>C<sub>β</sub>-C<sub>4</sub></b>					1.523	1.512		
	<b>S<sub>1</sub>-C<sub>m</sub></b>	1.827	1.826	1.826	1.832			1.825	1.824
	<b>C<sub>4</sub>-C<sub>m</sub></b>					1.527	1.527		
	<b>d<sub>spin</sub>C<sub>β</sub></b>	0.00	0.00	-0.00	-0.00	-0.00	-0.00	-0.00	0.00
	<b>d<sub>spin</sub>C<sub>2</sub></b>	0.85	1.08	0.72	0.82	0.83	0.82	0.88	1.07

**Kinetics:** To explore the effect of substituents on the addition-fragmentation rate coefficients in RAFT polymerization, rate coefficients at 25°C were calculated at DFT level with the same functional used for the thermodynamics of the reactions.

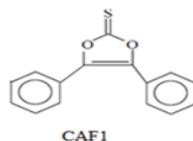
**Table.5. Calculated rate coefficients for addition ( $k_{add}$ )( $L \cdot mol^{-1} s^{-1}$ ) fragmentation ( $k_{frag}$ )( $s^{-1}$ ) reactions at 298.15K**

	$k_{add}$		$k_{frag}$	
<b>M1</b>	6.65	$10^9$	<b>RM1</b>	$8.19 \cdot 10^{27}$
<b>M2</b>	2.56	$10^{15}$	<b>RM2</b>	$1.87 \cdot 10^{-11}$
<b>M3</b>	7.74	$10^9$	<b>RM3</b>	$0.30 \cdot 10^{11}$
<b>M4</b>	3.91	$10^{16}$	<b>RM4</b>	$4.39 \cdot 10^8$
<b>M5</b>	4.72	$10^{27}$	<b>RM5</b>	$1.95 \cdot 10^{17}$
<b>M6</b>	5.62	$10^6$	<b>RM6</b>	$6.49 \cdot 10^7$
<b>M7</b>	1.83	$10^{21}$	<b>RM7</b>	$2.82 \cdot 10^{17}$
<b>M8</b>	5.56	$10^{17}$	<b>RM8</b>	†

From the results reported in Table 5, we see the addition reaction is a relatively fast, only for M6 which present a transition state( smallest  $k_{add}$ ) and monomers have a reactive C=S double bond (high  $k_{add}$ ) then we have an efficient RAFT polymerization (Moad, 2005). It is apparent that the addition rate coefficients significantly depend on the nature of the substituents on the agents used, since they differ by 21 order of magnitude over the reactions considered at B3LYP level of theory.

**TDDFT calculations:** Further to the thermodynamic and kinetic results obtained for the molecule M4 and CAF1 (scheme 2); we judge interesting to compare their electronic spectra as well as their radical adducts.

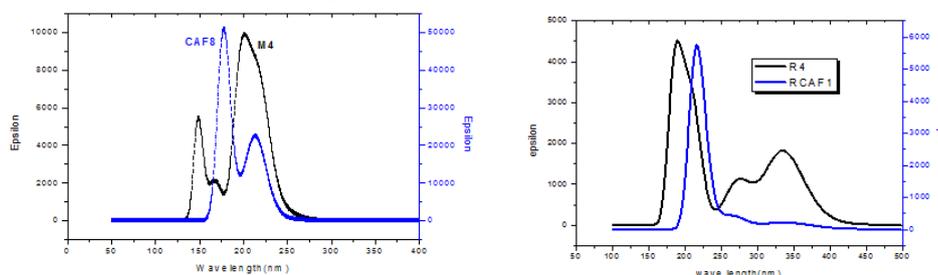
In recent years, TDDFT has emerged as a reliable standard tool for the theoretical treatment of electronic excitation spectra and recent works demonstrate the good accuracy for a wide range of systems (Parac, 2002; Fabian, 2001). In this section we present and discuss the results of the vertical electronic transitions computed at the optimized geometries of singlet ground electronic state in the gas phase; using the same program package both of CAF and his model. The model presents the same nature of transitions that in CAF.



**scheme 2**

By creating molecular chains with alternate  $\pi$  bonds, absorption can be shifted to longer wavelengths. In these so-called  $\pi$ -conjugated molecules, the electrons are delocalized over the whole  $\pi$  system. Therefore, by increasing the length of the molecule, the  $\pi$ -electrons become more delocalized, and the HOMO-LUMO energy gap decreases (Lopez, 2006) and it is the case of two molecules CAF1 and M4 which present a 0.151eV reduction in the energy gap when we substituted the two phenyls of CAF1 by two CN in M4. So the electrons are more delocalized in M4 than in CAF1 (confirmed by lengths bonding:  $M4 < CAF1$ ). The representation of the HOMO of the two molecules shows a strong  $\pi$  character with a delocalized electron density on the C = S while the LUMO of the two molecules have a  $\pi^*$  character and are delocalized over the entire molecule as shown, resulting an intramolecular charge transfer (ICT) from the Homo to the Lumo. The two substituents C $\equiv$ N have the same contribution as the phenyls.

The comparison of their spectra shows that the thionocarbonates absorption range, of the two molecules, is the same and that modeling CAF1( $\epsilon \sim 50000$ ) by M4( $\epsilon \sim 10000$ ) greatly reduces the intensity of absorption and then gives the hypochromic effect, as shown in Figure 3.



**Figure.3. Calculated Absorption Spectra of CAF1, RCAF1, M4 and RM4.**

For the molecule M4 we observe a maximum absorption at 197 nm given by both transitions H-1  $\rightarrow$  Lumo whose contribution was 30% (34% in the CAF1) and H-1 to L + 2 with 57% of contribution. The shoulder at 219nm ( $f = 0.1423$ ) is also due to 47% of the transition H-1 to Lumo. The peak at 148nm ( $f = 0.079$ ) of the M4 molecule is a transition Homo  $\rightarrow$  Lumo + 6 (68%).

The two highest transitions are not of the same nature but they have the same type of character:  $\pi \rightarrow \pi^*$  with lower energy gap in M4 (6.807eV) than in CAF1 (6.923eV).

The electronic spectra of adduct radicals: RM4 and RCAF1 reported also in Figure 3 show that RM4 radical absorb better in the region (near UV) (347nm) due to the transition Homo---Lumo. The two adduct radicals RM4 and RCAF1 show a CT at this transition (Homo to Lumo) (347nm and 361nm respectively). In addition, RM4 present a charge transfer at the maximum absorption which we don't see in the RCAF1.

#### 4. CONCLUSION

The DFT calculation showed that the RAFT reaction of thionoesters compounds in cyanomethyl radical polymerization may be rather difficult ( $\Delta G1 > 0$  for the addition mechanism) contrarily to the methyl and styryl radical polymerizations ( $\Delta G1 < 0$ ). This result can be attributed to the fraction of transferred electron ( $\Delta N^e$ ) and the difference of electrophilicity ( $\Delta\omega$ ) between R2 and the thionoesters. These parameters indicate a large polar character (highest values) for this radical addition mechanism as compared to the addition of R1/thionoester and R3/thionoester, respectively. From the mechanistic point of view, it is favorable to model the CAF1 by M4. For TDDFT study, it is clear that for this series of thiocarbonyls, the models possess the same shape of the spectrum that CAF and the same absorption range with a slight displacement.

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